

MULTILAYER POLYMERIC/ZERO VALENT MATERIAL
STRUCTURE FOR ENHANCED GAS OR VAPOR BARRIER AND UV
BARRIER AND METHOD FOR MAKING SAME

5 Technical Field

 This invention relates to multilayer structures comprising a polymeric layer and an inorganic gas or vapor barrier layer or ultraviolet light barrier layer or both. More particularly, this invention relates to plastic beverage containers and enhancing the gas or vapor barrier and UV light barrier properties of the container. Still more particularly, this invention is particularly applicable to PET structures, such as rigid PET containers.

 Background of the Invention

 Polymeric materials have numerous advantages as packaging materials for food and beverages. They are lightweight, impact resistant, and easily shaped. Accordingly, they have enjoyed widespread popularity. Unlike glass and metal, however, all polymers exhibit a measurable degree of permeability to gases and vapors. This deficiency inherently limits the use of polymers in more demanding applications, especially where oxygen ingress or carbon dioxide loss affects the quality of the contained food or beverage.

 Numerous technologies have been developed to decrease the permeability of polymers, and thus increase their range of applicability to food and beverage packaging. One of the most promising approaches has been the deposition of thin layers of inorganic oxides on the surface of the polymers, either prior to or after mechanically forming the polymer into the finished container. Inorganic oxides, especially silicon dioxide, have been explored extensively, because of their transparency, impermeability, chemical inertness, and compatibility with food and beverages.

 Inorganic oxides can be deposited onto a polymeric surface by a number of techniques, including sputtering and various types of vapor deposition including plasma vapor deposition, plasma enhanced chemical vapor deposition, and electron beam or anodic arc evaporative vapor deposition. Although each technique has its own advantages and disadvantages, they all allow the deposition of nanometer-thick layers of

the oxide onto the preformed polymer surface. Because of the thinness of the layer, the resulting structures retain most of the physical properties of the base polymer, but can exhibit reduced permeability.

5 Despite this, commercialization of containers based on polymeric/inorganic oxide multilayer structures has been slow, and is mostly limited to flexible containers made by post-forming coated films. In particular, rigid polymeric containers with inorganic oxide coatings have proven difficult to develop. This is because that, although the deposition of inorganic oxides onto the surface (especially the exterior surface) of a rigid container is not difficult to accomplish, heretofore those containers have not exhibited sufficient
10 reductions in permeability over the uncoated containers. This is in spite of the fact that the inorganic oxide coating is typically deposited over the entire surface of the rigid container.

The reason for this modest decrease in permeability (permeability decrease is equivalent to barrier increase) is due to the presence of residual pinholes in the inorganic
15 oxide layer. Pinholes are created in part by pressurization of containers, such as when containers hold carbonated beverages. The surface area occupied by these pinholes is usually quite small (on the order of less than 1% of the total surface); however, the impact of these pinholes is far greater than their surface area would suggest. This is because diffusion through a polymer occurs in all three spatial dimensions; thus, each pinhole can
20 drain a much larger effective area of the container surface than the actual area occupied by the pinhole.

Because the surface of rigid containers is inherently less smooth than the surface of biaxially oriented films, the pinhole density on coated containers is much greater than that for films. Thus, whereas barrier improvements of 10-100x are possible when
25 biaxially oriented PET film is coated with silicon dioxide; barrier improvements of only 2-3x have been obtained when rigid PET containers are similarly coated and used to hold carbonated beverages. This reduced barrier improvement is due in part to pressurization of the container. In addition, when the silicon oxide layer is on the external surface, it is subject to mechanical degradation on handling of the container, such as that which occurs
30 in normal package filling operations.

Numerous methods have been explored to address this problem. The most common approach has been to deposit thicker layers of the oxide; however, this approach is inherently self-defeating. Thicker layers are less flexible and less extensible than thin layers, and therefore more prone to fracturing under stress. Another method is to apply multiple layers of inorganic oxides, sometimes with intermediate processing to redistribute the pinhole-causing species. This approach also has met with little success, in part because of the greater complexity of the process, and because of its modest impact on barrier improvement. A third method has been to supply an organic sub-layer on the polymer surface to planarize the surface and cover up the pinhole-causing species prior to laying down the inorganic oxide. This method also greatly increases the complexity and cost of the overall process, and similarly only affords modest improvements in barrier performance. A fourth approach has been to melt-extrude a second polymer layer on top of the inorganic oxide layer, and thus provide additional resistance to gas flow through the pinholes. Thus, Deak and Jackson (Society of Vacuum Coaters, 36th Annual Technical Conference Proceedings, 1993, p318) report that applying a 4 micron layer of poly(ethylene-co-vinyl acetate) on top of a PET/SiO_x structure improved the barrier property by 3x, and applying a 23 micron top layer of PET improved the barrier performance by 7x.

Despite the barrier improvement demonstrated by Deak and Jackson, there has been little commercial implementation of this approach, for several reasons. First, melt extrusion of a second polymer onto a polymeric/inorganic oxide film imparts substantial thermal stress to the preformed structures, often severely compromising their barrier performance. Second, structures where the two polymers are different are inherently more difficult to recycle than structures composed only one polymer. Third, coextrusion of a second polymer onto preformed rigid containers is nearly impossible with current technology, and is cost prohibitive for large volume applications in the food and beverage industry.

Transmission of ultraviolet light through plastic food or beverage containers can also affect the quality of the contained food or beverage. Ultraviolet light causes off-taste in many beverages such as water, juice and beer. Clear plastic containers such as clear PET bottles transmit virtually 100% of ultraviolet light. One solution to this problem is

tinting the plastic with a colorant which blocks UV light. Colored plastic containers, however, are difficult to recycle because they would discolor otherwise clear plastic during recycling.

Thus, there is a need for polymer/inorganic multilayer structures with enhanced
5 gas or vapor barrier or UV barrier or both, especially PET containers with such enhanced barrier.

Summary of the Invention

This invention solves the above-described problems in the prior art by providing a
10 coated multilayer structure comprising a polymeric base layer, a zero valent material barrier layer, and a top coat on the zero valent material barrier layer comprising a soluble compound capable of reducing the permeability of the multilayer structure to gas or vapor. More particularly, the soluble compound has a plurality of carboxyl, hydroxyl, or carboxamide functional groups, has a melting point above room temperature (25 °C), is
15 chemically non-reactive with the inorganic barrier coating, is water soluble, and is nontoxic. It is also preferable that the solution containing the soluble compound exhibits good wettability with the inorganic coating. The soluble compound of the top coat blocks ingress or egress of gas or vapor through pores or pinholes in the zero valent material barrier layer. The top coat is particularly suitable for blocking ingress or egress of
20 oxygen and carbon dioxide.

Suitable zero valent materials include elemental silicon and elemental metals such as aluminum, nickel, chromium, and copper. Under some circumstances, it may be desirable for the zero valent material barrier layer to be a barrier to the transmission of ultraviolet light. Desirably for some applications, the multilayer structure has an
25 ultraviolet light transmission of less than 5%. A silicon coating, for example, provides ultraviolet light barrier.

This invention also encompasses a coated multilayer structure comprising a polymeric base layer and a zero valent material barrier layer, wherein the zero valent material barrier layer is a barrier to transmission of ultraviolet light. According to one
30 embodiment, this coated multilayer structure can further comprise an inorganic oxide gas barrier layer and, in addition, a top coat as described above.

In addition, this invention encompasses a method for enhancing the gas or vapor barrier properties of a multilayer structure comprising a polymeric base layer and a zero valent material barrier layer. This method comprises applying to the zero valent material barrier layer a top coat comprising the above-described soluble compound. Desirably, the soluble compound is applied to the zero valent material barrier layer in a form of a solution such as an aqueous solution. The multilayer structure is allowed to dry such that the solvent evaporates and the soluble compound remains as a top coat.

The soluble compound of the top coat can be polymeric or monomeric. Suitable polymeric compounds for the top coat include carboxymethyl cellulose, polyacrylamide, polydextrose, polyacrylic acid, and polyvinyl alcohol. Suitable monomeric compounds for the top coat include sucrose, caramel, and citric acid.

The treatment of this invention is particularly useful for enhancing the gas or vapor barrier and UV light barrier characteristics of containers such as food or beverage containers. This invention is particularly useful for enhancing the gas or vapor barrier and UV light barrier characteristics of packaged beverage containers such as carbonated soft drink, juice or beer containers. According to a particular embodiment, the top coat of this invention is applied to a silicon-coated polyethylene terephthalate container. This invention therefore also encompasses food and beverage containers comprising the enhanced barrier multilayer structure of this invention. Because of the enhanced gas or vapor barrier and UV light barrier, the container of this invention preserves the quality of food or beverage in the container and prevents off-taste in such food or beverage.

This invention further encompasses a method for producing recycled content plastic comprising providing a batch plastic, at least a portion of the batch plastic including a coated multilayer structure comprising a polymeric base layer and a zero valent material barrier layer on a surface of the polymeric base layer, chemically removing the zero valent material barrier such as with caustic, and converting the batch plastic to a form suitable for melt extrusion. Desirably, the zero valent material barrier layer is a barrier for transmission of ultraviolet light. By chemically removing the zero valent material barrier, the remaining polymeric base layer is substantially clear of colorant and can be recycled with other substantially clear plastic.

Other objects, features and advantages of this invention will be apparent from the following detailed description of embodiments, claims, and drawings.

Brief Description of Drawings

5 Fig. 1 is an elevation view of a packaged beverage including a container coated with a gas or vapor barrier top coat in accordance with an embodiment of this invention.

 Fig. 2 is a partial sectional view of the container in Fig. 1 illustrating the multilayer structure of the container.

10 Fig. 3 is a graph illustrating the UV light transmission of an Si-coated PET container and an uncoated PET container.

Detailed Description of Embodiments

 As summarized above, this invention encompasses multilayer structures comprising a polymeric base layer and a zero valent material barrier layer, and a top coat
15 on the zero valent material barrier layer for reducing the permeability of the multilayer structure to gas or vapor and thereby increasing barrier of the multilayer structure to gas or vapor. Sometimes it is desirable for the zero valent material barrier layer to be a barrier to UV light as well. This invention also encompasses a method for reducing the permeability of such a multilayer structure to gas or vapor and a method for recycling
20 multilayer structures.

 Polymeric-inorganic multilayer structures with enhanced gas or vapor barrier and UV light barrier properties are particularly useful as food or beverage containers. It is often desirable that food or beverage containers prevent oxygen ingress or carbon dioxide egress. For example, polymeric containers with an enhanced vapor or gas barrier coating
25 are desirable as packaged beverage containers and are particularly useful as carbonated beverage or beer containers because they retain carbon dioxide and prevent oxygen ingress better than plastic containers without an enhanced vapor or gas barrier coating.

 Fig. 1 illustrates a packaged beverage 10 comprising a container body 12, a beverage (not shown) disposed in the container, and a closure or cap 16 sealing the
30 beverage within the container body. Fig. 2 illustrates the multiple layers of the container body including the polymeric base layer 18, the zero valent material gas or vapor barrier

layer 20 on the exterior surface 22 of the base layer, and a vapor or gas barrier enhancing top coat 24 on the zero valent material barrier layer. The layers are arranged such that the zero valent material layer 20 is between the exterior surface 22 of the base layer 18 and the top coat 24. The top coat 24 illustrated in the Fig. 2 is continuous on the surface of the zero valent material barrier layer, but can be discontinuous. The top coat 24 is applied so as to enhance the vapor or gas barrier of the multilayer structure container 12.

Suitable polymers for forming the polymeric base layer 14 of the multilayer structure container 12 can be any thermoplastic polymer suitable for making containers. Polyesters are particularly suitable and polyethylene terephthalate (PET) is commonly used to form beverage containers. Other suitable polyesters include polyethylene naphthalate (PEN), PET/PEN blends, PET copolymers, and the like. Although this invention is applicable to flexible containers, it is most effective on substantially rigid containers.

The zero valent material barrier layer 20 can reduce the permeability of the container 10 to gas and vapor, particularly carbon dioxide and oxygen, or can reduce the transmission of UV light through the container, or both. Silicon (Si) is particularly desirable for some beverage containers because it is an effective UV light barrier, provides some gas or vapor barrier, and is chemically inert and compatible with food and beverages. Other suitable zero valent materials include elemental metals such as chromium, nickel, aluminum, and copper.

The zero valent material barrier layer 20 can be applied to the polymeric base layer 14 by a number of techniques including sputtering and various types of vapor deposition including plasma vapor deposition, plasma enhanced chemical vapor deposition, and electron beam or anodic arc evaporative vapor deposition. Suitable vapor deposition techniques are disclosed in U.S. Patent Application Serial No. 09/380,904, filed on September 10, 1999, and corresponding to International PCT Application PCT/US98/05293, and U.S. Patent Application Serial No. 09/128,456, filed on August 3, 1998, and corresponding to International PCT Patent Application PCT/US99/15828, the disclosures of which are hereby expressly incorporated herein by reference. These zero valent material barrier layers often have pores or pinholes which allow passage of gas and vapor.

Anodic arc evaporative vapor deposition is a particularly desirable method of applying the zero valent material barrier layer 20 to the polymeric base layer 14 and for applying any additional gas or vapor barrier layers such as an SiO_x layer. In an anodic arc vapor deposition system, a solid material such as silicon is heated in a vacuum cell so as to release silicon vapor in the vacuum cell. An electric arc discharge system is also disposed in the vacuum cell and includes an anode and a consumable cathode comprising a vaporizable solid. The anode and cathode of the electric arc discharge system are charged with a source of DC current such that an electric arc discharge develops between the anode and the cathode. Sufficient voltage and current are applied to vaporize the solid cathode and form an energized vapor or plasma comprising ionized particles. This plasma formed by the electric arc discharge mixes with the silicon coating vapor evaporated in the vacuum cell to form an ionized coating plasma comprising silicon and the evaporated cathodic material, which can be a dopant, if desired. Containers to be coated are exposed to the ionized coating vapor within the vacuum cell and the coating vapor deposits a solid coating onto the outer surface of the containers.

The top coat 24 reduces the permeability of the container 12 to gas or vapor. Suitable soluble compounds for forming the top coat are solid at room temperature (25 C) and pressure (atmospheric pressure). Desirably, the top coat comprises a water soluble compound containing a large portion of hydroxyl groups, carboxamide groups or carboxylic acid groups for optimal barrier improvements. It is also desirable that the soluble compound for forming the top coat is non-toxic and chemically nonreactive with the zero valent material barrier layer. It is also preferable that the solution containing the soluble compound exhibits good wettability with the inorganic coating.

The top coat can be applied by dissolving the soluble compound in water or another suitable solvent and applying the solution to the zero valent material barrier layer of the container by suitable means such as dipping or spraying. When the solvent evaporates, the soluble compound remains in the pores or pinholes of the zero valent material barrier layer to block ingress or egress of gas or vapor.

Although there are many solid/solvent combinations that are effective in the operation of this invention, it is preferred that both the solid and solvent be compatible

with food and beverages. It is particularly preferred that both the solid and solvent have regulatory approval for use in food-contact. It is especially preferred to use water as the solvent, due to its low cost, non-toxicity, and ease of handling. There are many candidate solids, both polymeric and non-polymeric, that are water soluble, and that are acceptable for food contact. Examples of non-polymeric materials that can improve the barrier performance of polymeric structures include sucrose, caramel, and citric acid. Examples of suitable soluble polymeric materials for forming the top coat include carboxymethyl cellulose, poly(acrylamide), polydextrose, poly(acrylic acid), and poly(vinyl alcohol).

Higher concentrations of the soluble solid top coat compound normally afford greater barrier enhancement, but the barrier enhancement levels off eventually as concentrations of the soluble solid top coat compound increase. In contrast, higher molecular weight polymers are not more effective than low molecular weight compounds. Accordingly, it is preferable to employ a higher concentration of a low molecular weight compound, rather than a low concentration of a higher molecular weight compound.

The thickness of the top coat may vary and can be very thin. Some top coats can be applied at a thickness of 50 microns or less and some can be applied at a thickness of 10 microns or less. It should be understood, however, that the thickness of the top coat can be greater than 50 microns.

Specific embodiments of barrier-enhancing treatments of this invention include dipping Si-coated PET bottles into an aqueous carboxy methyl cellulose (CMC) solution followed by evaporation of the water, or dipping Si-coated PET bottles into aqueous solutions containing poly-vinyl alcohol polymers. When similar operations are performed on PET that lacks a coating of Si, no barrier improvements are observed. It is notable that this effect can be reversible; thus, when a Si-coated PET bottle that has been previously treated with a carboxy methyl cellulose solution is immersed momentarily in pure water, the barrier enhancement disappears.

In some embodiments, application of the top coat to uncoated polymeric structures such as plastic bottles can enhance gas barrier of the polymeric structures. In direct application of the top coat to polymeric structures, better results are obtained if the uncoated polymeric structure is wettable with the top coat solution. Generally, however,

the combination of an inorganic oxide barrier layer with a top coat provides much greater gas barrier.

An additional benefit of this invention is that, in addition to enhancement of the barrier properties of coated polymeric structures, it provides a method to increase the abuse resistance of such structures. Specifically, if film-forming polymeric materials are dissolved in the solution, deposition of those polymers onto the surface of the zero valent material barrier layer can increase the abuse resistance of that layer. This is particularly useful in manufacturing packaged beverages because of the necessary mechanical handling of the treated containers.

In the manufacture of packaged beverages, the top coat of this invention can be applied to containers in a continuous packaged beverage manufacturing line between application of the zero valent material barrier layer to the container and filling the container with the beverage. Alternatively, the top coat can be applied to the containers after they are filled with beverage. Regardless, the containers treated in accordance with this invention can be used to manufacture packaged beverages in a conventional packaged beverage manufacturing facility.

It should be understood, that the top coat 24 may not be desired in some circumstances and can be left off of the container if the zero valent material provides sufficient barrier for the particular application. Alternatively, the container can be coated with both a layer of zero valent material and a layer of inorganic oxide gas barrier material such as SiO_x . Both layers can be deposited by sputtering or various types of vapor deposition as described above. A top coat can then be applied such that the layer of zero valent material and the layer of inorganic oxide gas barrier material are between the polymeric base layer and the top coat.

Zero valent materials are often colored; however, plastic containers such as PET bottles coated with colored zero valent material such as silicon are recyclable with other substantially clear plastic by chemically removing the zero valent material barrier layer from the container. Caustic is one effective means for chemically removing the zero valent material barrier layer. After removal of the zero valent material barrier layer, the plastic container can be mixed with other substantially clear plastic material and converted to a form suitable for melt extrusion such as by grinding the batch plastic to

produce flakes and melting flakes to form a melt extrudable recycled plastic or depolymerizing the batch plastic and repolymerizing the depolymerized batch plastic to form a melt extrudable recycle plastic.

5 EXAMPLES

In the following examples, Si-coated and Si/SiO_x coated PET bottles were subjected to various treatments that demonstrate the barrier-enhancing effect of the present invention. These examples are intended to illustrate particular embodiments of this invention, but not limit the scope of this invention. In these examples, the CO₂ loss rate was measured by determining the rate that CO₂ migrated to the exterior of the bottle, when the bottles were pressurized to 5 bar pressure and held at 38 °C. The barrier improvement factor (BIF) was determined by measuring the loss rate for the barrier-coated bottles treated with a top coat vs. the loss rate for bottles without a barrier coat or a top coat. For example, the BIF of a plain, uncoated PET bottle is 1. Assuming the shelf life of a carbonated beverage packaged in a plain, uncoated PET bottle is about 10 weeks, the shelf life of a carbonated beverage in a coated PET bottle having a BIF of 1.2 would be about 12 weeks, the shelf life of a carbonated beverage in a coated PET bottle having a BIF of 2 would be about 20 weeks, and the shelf life of a carbonated beverage in a coated PET bottle having a BIF of 20 would be about 200 weeks.

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Examples 1- 8

Eight 500 ml PET bottles produced by commercial stretch-blow molding were exterior-coated with a 50 nanometer layer of Si, using an anodic-arc plasma vapor deposition process. The PET bottles were dipped into a 5% aqueous solution of low molecular weight carboxymethyl cellulose, and allowed to air dry. The BIF of each container after coating with Si was determined and the BIF of each container after application of the CMC top coat was determined. These values are set forth in Table 1. As can be seen, both the application of the Si coating and the top coat enhanced the gas or vapor barrier of the container. The UV light barrier of an Si-coated PET container is illustrated in Fig. 3.

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TABLE 1

	<u>Example</u>	<u>BIF After Si Coating</u>	<u>BIF After Top Coat Over Si Coating</u>
	1	1.96	8.81
	2	1.32	6.26
5	3	1.44	11.15
	4	1.28	7.32
	5	1.44	20.10
	6	1.28	9.88
	7	1.38	13.75
10	8	1.43	16.97

Example 9

The Si-coated bottles of Example 7 were dipped in clean tap water for 30 seconds, then were removed and allowed to air-dry. The BIF was again measured. The measured BIF was 1.84.

Example 10

Si-coated bottles with a BIF of 2.13 were dipped into a 5 % aqueous solution of polyacrylamide and allowed to air dry. It was observed that the solution did not wet the surface as well as the CMC. After this treatment, the measured BIF was 4.91.

Example 11

Si-coated bottles with a BIF of 1.79 were dipped into a 5 % aqueous solution of polyvinyl alcohol and allowed to air dry. It was observed that the solution did not wet the surface as well as CMC. After this treatment, the measured BIF was 3.64.

Example 12-15

500 ml PET bottles produced by commercial stretch-blow molding were exterior-coated with a layer of aluminum, using an anodic-arc plasma vapor deposition process. The PET bottles were dipped into a 5% aqueous solution of low molecular weight carboxymethyl cellulose, and allowed to air dry. The BIF of each container after coating

with aluminum was determined and the BIF of each container after application of the CMC top coat was determined. These values are set forth in Table 2. As can be seen, both the application of the aluminum coating and the top coat enhanced the gas or vapor barrier of the container.

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TABLE 2

<u>Example</u>	<u>BIF After Al Coating</u>	<u>BIF After Top Coat Over Al Coating</u>
12	3.26	9.8
13	2.74	5.56
10 14	2.99	8.37
15	2.68	12.07

Example 16

500 ml PET bottles produced by commercial stretch-blow molding were exterior-coated with a layer of Si followed by a layer of SiO_x, or exterior-coated with a layer of SiO_x followed by a layer of Si, using an anodic-arc plasma vapor deposition process for both layers. The coated bottles also provided UV protection. The PET bottles were dipped into a 5% aqueous solution of low molecular weight carboxymethyl cellulose, and allowed to air dry. The BIF of each container after coating with Si and SiO_x was determined and the BIF of each container after application of the CMC top coat was determined. These values are set forth in Table 3. As can be seen, both the application of the Si/SiO_x coating and the top coat enhanced the gas or vapor barrier of the container.

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TABLE 3

Si/SiO₂ multi-layered bottles + top coat

Treatment	BIF before top coat	BIF after top coat
40nm Si + 10nm SiO ₂	1.72	12.71
40nm Si + 10nm SiO ₂	1.27	19.99
40nm Si + 10nm SiO ₂	1.84	16.16
40nm Si + 10nm SiO ₂	1.50	10.96
30nm Si + 20nm SiO ₂	1.68	11.67
30nm Si + 20nm SiO ₂	1.72	9.32
30nm Si + 20nm SiO ₂	2.03	8.80
30nm Si + 20nm SiO ₂	1.84	11.49
20nm Si + 30nm SiO ₂	2.14	11.48
20nm Si + 30nm SiO ₂	1.69	10.19
20nm Si + 30nm SiO ₂	2.23	8.70
20nm Si + 30nm SiO ₂	1.84	7.50
10nm SiO ₂ + 40nm Si	1.60	11.58
10nm SiO ₂ + 40nm Si	1.90	19.71
10nm SiO ₂ + 40nm Si	1.99	13.13
10nm SiO ₂ + 40nm Si	1.97	21.56
20nm SiO ₂ + 30nm Si	2.23	17.01
20nm SiO ₂ + 30nm Si	1.92	14.17
20nm SiO ₂ + 30nm Si	2.04	13.33
20nm SiO ₂ + 30nm Si	2.00	13.60
30nm SiO ₂ + 20nm Si	1.97	8.27
30nm SiO ₂ + 20nm Si	2.02	11.32
30nm SiO ₂ + 20nm Si	2.28	8.12
30nm SiO ₂ + 20nm Si	2.14	11.22

5 The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

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